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# **Improved IR Windows for Severe Aerothermal Environments**

Phase I Final Technical Report  
Contract Number: # N00167-04-C-0018

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Issued By:  
Naval Surface Warfare Center, Carderock Division  
Attn: Code 3322 (L. Rider)  
9500 MacArthur Blvd.  
West Bethesda, MD 20817-5700

Prepared by:  
**Technology Assessment and Transfer, Inc.**  
133 Defense Hwy. Suite 212  
Annapolis, MD 21401  
(410) 224-3710

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## 1. Introduction

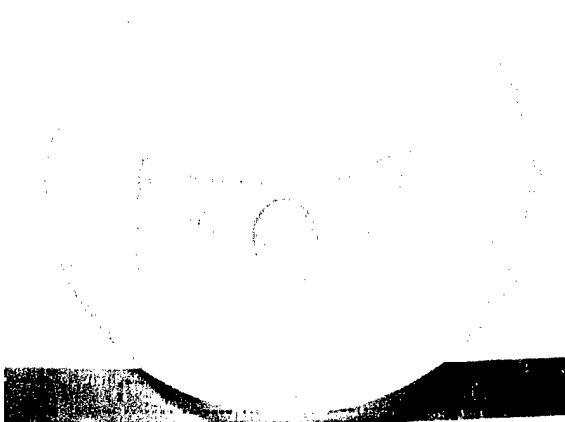


Figure 1: Unpolished dome blank produced at TA&T as a result of this Phase I effort.

(unpolished condition), the target delivered cost is less than approximately \$1,000. These cost ceilings, which have been designated for each of the sub-components, are driving much of the materials selection process at this time, and transparent spinel is favored as a durable, broadband, electro-optical dome material that is capable of meeting these goals. Production approaches are therefore being pursued to establish a robust, low-cost fabrication technology to deliver spinel domes with excellent optical properties that require minimal finishing.

Technology Assessment & Transfer Inc., (TA&T) has been aggressively developing a pressureless sintering approach for the JCM spinel domes as a reliable, scalable, high-volume, low-cost manufacturing method. One key that has always been known as a cornerstone to successful pressureless sintering of transparent domes has been the availability of a reliable, high-purity spinel powder. Initial work began under an IR&D funded effort, where a multi-phased approach was initiated to address the manufacturability of spinel domes. This approach investigated exploratory methods to establish suitable raw materials, followed by refinement of processing techniques at the coupon level, and finally the transfer of this technology to the fabrication of 3.5 inch and 7 inch diameter domes. One of these unpolished dome blanks is shown in Figure 1. These technology development and transfer efforts were supported by

### 1.1 Background

The Joint Common Missile (JCM) program, led by the US Army, is the next generation air-to-ground missile that will be carried on a wide range of Army, Navy, and Marine Corps fixed and rotary wing platforms. JCM is designed to replace the Longbow/Hellfire missile on the Apache, Cobra, and Seahawk helicopters and the Maverick missile on the F/A-18, and will be phased in over a period of several years. The long-term U.S. production run is estimated at 54,000 missiles with additional units likely being produced for foreign military sales. Cost is one of the key drivers in component/system selection criteria. For the targeting dome blank

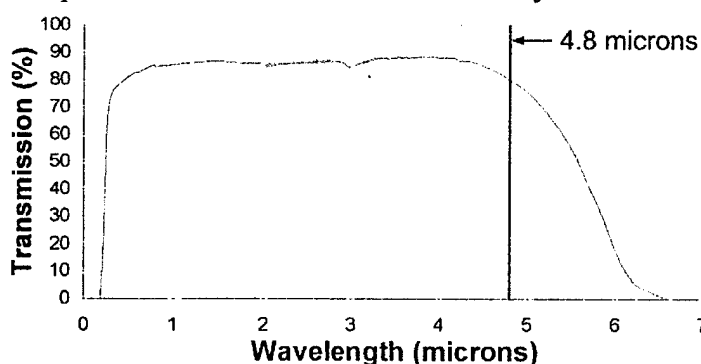


Figure 2: Full spectrum transmission curve through the mid-wavelength infrared region. This sample was sintered at 1550°C for 2 hours, and the polished thickness was 3.5 mm. Transmission is near the theoretical limit for spinel from the UV to the mid-IR.

the Army and from the Navy under separate SBIR programs, which as this report elucidates, were instrumental in our success. As a result, TA&T has worked closely with raw material suppliers to tailor the spinel powder for pressureless sintering fabrication. This has necessitated multiple powder lots and iterations at every stage of the processing.

*In a program to enhance the fabrication process for the production of spinel domes, TA&T has evaluated a variety of spinel powders for pressureless sintering. The effects of powder blending and milling, cold isostatic pressing conditions, binder removal, sintering, and hot isostatic pressing on the final transparency of pressureless sintered parts have been determined. A working knowledge of the processing window has been established, allowing transparent spinel domes to be produced on a repetitive basis. This report details these investigations of the processing variables, and documents the successes of the Phase I effort.*

## **2. Objectives and Accomplishments**

Several promising developments resulted during this Phase I program, including the fabrication of several transparent 7 inch diameter domes. This achievement was comprised of many individual accomplishments, which are summarized below.

### **2.1 Fabrication of Transparent 7 inch Diameter Domes**

The main objective and accomplishment has been the fabrication of several transparent 7 inch diameter full hemisphere domes. Through rigorous experimentation at every stage of processing, TA&T, the Army Research Laboratory, and Northrop-Grumman have jointly arrived at an understanding of the processing conditions necessary to produce uniform transparent spinel domes. While these processing steps and conditions are not yet optimized, structurally sound and transparent domes can be reproducibly fabricated.

**Conclusion: Rigorous experimentation has produced a processing schedule for fabricating uniformly transparent 7 inch diameter spinel domes.**

### **2.2 Coupon Level Testing of Binders**

Generally, organic binders are added to powder mixtures to aid in uniform densification and to add strength to the green pressed part. CIPing of 3.5 inch diameter green domes has already been successfully performed without the addition of a binder (detailed later in this report) and the blanks were found to have sufficient strength in their green form to withstand normal handling at this size. However, some crumbling was observed around the circumference of the domes. At a similar thickness and at twice the size, the 7 inch diameter domes did not have sufficient strength to withstand normal handling without the addition of a binder. The need for some type of binder is clear, and this may be accomplished either by introduction through the spray drying process, or through introduction of a binder by milling. In advance of development work on 7 inch domes with the spray dried powder, a coupon level study was initiated on 2.5 inch uniaxially pressed disks. The various binders prescribed in Task 2 have been milled with spinel powder for the required length of time and pressed into disks. These disks have been isostatically pressed (CIPed), sintered according to prescribed schedules, and hot isostatically pressed (HIPed) at the U.S. Army Research Laboratory (ARL). The experimental results

revealed that the most optically transparent parts were produced without binder, but the samples that contained PEG 4000 binder exhibited the best green strength and optical clarity following HIPing. For pressing of domes, this will be the alternative binder choice.

**Conclusion: Pressing of 3.5 inch diameter domes was accomplished without binder, but larger 7 inch diameter domes could not be pressed without binder. Spray dried powder obtained directly from Baikowski contains a proprietary binder. PEG 4000 exhibited the best clarity and pressing characteristics and will be considered as an alternative binder choice.**

### **2.3 Coupon Level Testing of Sintering Aids**

Despite many studies previously performed investigating a variety of sintering aids, their role in producing optically transparent domes by pressureless sintering is not fully understood. The use of sintering aids, such as LiF, has proven to be critical in hot pressing of transparent spinel. In this work, a separate study was initiated to test how sintering aids affect the overall sintering behavior, resulting density and optical transparency. The desired LiF concentrations listed in Task 3 have been milled with spinel powder, and uniaxially pressed into 2.75 inch disks. These disks were CIPed, sintered, and HIPed at the ARL. Using the standard sintering cycles, the addition of LiF consistently degraded the optical clarity of all coupon samples. Based upon the consistently poor appearance of all samples with LiF additive, further studies using LiF as a sintering aid were discontinued.

**Conclusion: Disks with the required concentrations of LiF sintering aid in the range that proved successful in hot pressing of spinel exhibited generally worse optical clarity than samples pressed without LiF.**

### **2.4 Development of CIPing Protocol for 3.5 inch and 7 inch Diameter Domes**

Isostatic pressing of 3.5 inch diameter domes began in January. Methods and techniques for sealing and filling the 3.5 inch CIP dies have been standardized in a manner that enabled their use on 7 inch domes. The 7 inch domes have been consistently produced using these standardized techniques. For both the 3.5 inch diameter and 7 inch diameter domes, a standard load of powder was agreed upon based on the design requirements and tap density of the powder. A vibrating table, modified specifically to aid the dome mold filling operation, decreased the required time for loading the die cavity with powder by approximately two-thirds. A variety of experimental CIP conditions have already been explored. Three experimental CIP treatments were considered. CIP treatment A was performed with a single CIP treatment on a mandrel to a pressure of 30 ksi. CIP treatment B was performed by CIPing to an overall pressure of 15 ksi on a mandrel. CIP treatment C was performed by CIPing powder on a steel mandrel to 15 ksi, and reCIPing in a rubber balloon to a total pressure of 30 ksi. The presence of non-uniform stress gradients was inferred in parts pressed using CIP treatments B and C by the presence of severe cracking during binder removal (burnout) or sintering. Cycle A was determined to be the optimal CIP cycle.

**Conclusion: Several experimental CIP conditions have been tested, and a single CIP treatment to a pressure of 30 ksi on a mandrel proved optimal and resulted in parts that did not crack during sintering.**

## **2.5 Binder Removal Studies**

Over 7 wt % has been consistently removed during the binder removal/burnout studies from domes formed using spray dried Baikowski powder. In the spray dried powder, the weight loss is attributed to several factors. If the surface area is great enough, a portion of this weight loss may be attributed to desorption of adsorbed gases at increasing temperatures. The majority of adsorbed species to be removed from the powder during heating is water vapor adsorbed onto the surface of powder particles. For this reason, the powder should be stored in a low moisture environment whenever possible or practical. Lastly, there is an organic binder, and sometimes a plasticizer, added to assist the spray drying process. These additives are typically added to a maximum combined binder/plasticizer load of 5 wt%. In the spray dried powder used in this work, the total amount of organics added to this batch of powder was only 4 wt%. This weight percentage (double the normal binder load used by TA&T) necessitated extra tasks to determine optimum binder removal conditions for the spray dried powder. The standard binder removal schedule of holding at 700°C for 4 hours did not sufficiently remove the binder, and black specks were observed inside many of the early domes. Other conditions were tested, including 8 and 24 hour holds at 700°C to allow more time for complete removal of the binder. Significant improvements in dome clarity were observed using 8 hour holds at 700°C, but optical quality did not improve significantly when holding for longer periods of time. As a result, an 8 hour burnout hold at the maximum temperature of 700°C was selected as the optimum burnout schedule. This condition has been instituted as part of the standard sintering protocol.

**Conclusion: A comprehensive burnout/binder removal study was performed to determine the optimum conditions for removing the spray dried binder and producing parts with the highest optical clarity. A burnout of 700°C for 8 hours appears to be the minimum condition for complete removal of the binder for the spray dried powder.**

## **2.6 Sintering of Developmental 3.5 inch and 7 inch Diameter Domes**

Significant progress has been made towards determination of the optimum sintering conditions for producing optically transparent spinel domes. These sintering studies have led to a number of experimental profiles that have produced transparent domes. While the process is not optimized at this time, uniformly transparent domes have been consistently fabricated using these sintering profiles. Generally, these conditions include sintering to 1550°C with a 5°C/min or 2°C/min ramp rate to final temperature and 2°C/min cooling rate. These development level studies are detailed elsewhere in this report.

**Conclusion: The temperature protocols for sintering domes has not been fully optimized, several experimental sintering profiles capable of consistently producing transparent domes were found.**

## **2.7 Determination of Minimum HIP Conditions**

Strength limiting flaws scale with grain size in ceramic materials. Large average grain sizes or exaggerated grain growth can lead to significant decreases in the mechanical strength of spinel. Hot isostatic press conditions that have produced transparent spinel are typically above the temperature where rapid grain growth occurs. Therefore, HIPing is the determining factor in the overall grain size of the part. Different HIP temperatures have been tested in an effort to preserve a minimum grain size with the current sintering profiles. However, preservation of the grain size often occurs at the expense of the overall clarity. Several different maximum temperatures have been tested, and HIP cycles performed at 1650°C for less than 5 hours do not increase densification to optical clarity. However, the effect of time in densification at 1650°C has not been investigated, and the optimum condition may very well lie at this temperature for longer hold times. Furthermore, a combined sintering-HIPing matrix may identify sintering profiles that may initially appear to be inadequate, but produce excellent transparency after a lower than normal temperature HIP cycle. Thus far, of the conditions tested, HIPing at 1750°C for 5 hours appears to be optimum for producing optical clarity. HIPing at 1850°C for 5 hours causes substantial grain growth, which can further improve optical transparency, but at the obvious cost of reduced strength. As with the sintering behavior, HIPing protocols have not yet been fully optimized, and it is very possible that the optimum HIP cycle may include significantly longer processing times at even lower temperatures than have already been tested. However, conditions have been identified that produce optical clarity, and this was the main goal of the current investigation.

**Conclusion: Without investigating the effect of time or optimizing the HIP cycle, HIPing at 1750°C for 5 hours appears to be a more favorable treatment than HIPing for 5 hours at either 1650°C or 1850°C. HIPing at 1650°C or lower temperatures may still be viable, but only in conjunction with advances in other processing areas, such as refined sintering schedules.**

## **3. Contributors**

The following institutions participated in completion of the Phase I effort.

### **Technology Assessment and Transfer**

Technology Assessment and Transfer has provided coupon scale uniaxial press dies, 3.5 inch diameter and 7 inch diameter CIP dies, raw materials, and all binders and sinter aids. Personnel from TA&T travel to the Army Research Laboratory on a weekly basis to use the CIP to produce development domes or to isostatically press the coupon disks containing binder or sintering aids.

### **U.S. Army Research Laboratory**

Through a Cooperative Research and Development Agreement (CRADA) with TA&T, the U.S. Army Research Laboratory (ARL) has provided access to the cold isostatic press located at the Rodman Materials Laboratory. Isostatic pressing produces an overall increase in the green density of the pressed parts and reduces stress gradients within the parts versus uniaxial pressing. The uniform degree of powder compaction produced by isostatically pressing a dome shape

cannot be adequately replicated in a uniaxial press. Therefore, access to the CIP owned by the ARL and assistance in sintering and HIPing provided by Dr. Gary Gilde has been a critical factor in the success of this Phase I effort.

#### **Northrop-Grumman Corporation**

Northrop-Grumman has been a crucial member of the Phase I effort by providing sintering capability for several 7 inch domes and technical guidance in relaying the requirements of the seeker unit.

### **4. Experimental Methods**

A brief description of the experimental methods used in this Phase I work are contained below.

#### **4.1 Raw Materials – Spinel Powder**

In this work, three types of spinel raw material were used. A submicron-scale spinel powder from Sasol International Ceralox Division was used for the initial pressureless sintering trials. A suspected impurity problem produced orange/brown discoloration in the sintered-HIPed test coupons. As an alternative, a high surface area Baikowski powder from lot 21834 was used. This sub-micron scale powder does not flow or pack well in its as-received condition. In order to improve the die packing, quantities of this lot 21834 powder were also subjected to a spray drying process in which a slurry of powder, binder, and solvent was simultaneously sprayed and dried. The pre-agglomerated spheres of powder with incorporated binder flowed and packed more easily, and enhanced the compaction of the powder into the green part.

#### **4.2 Cold Isostatic Pressing**

Cold isostatic pressing (CIP) was performed in an Isomax 30 CIP manufactured by Engineered Pressure Systems, Inc. Multiple CIP treatments were tested through the course of this work, including a single pressing cycle on a mandrel to a total pressure of 15 ksi or 30ksi. Alternatively, a CIP/re-CIP cycle performed at 15 ksi on a mandrel, followed by a second CIP cycle at 30 ksi without a mandrel was also evaluated.

#### **4.3 Sinter Atmospheres and Conditions**

Multiple sintering furnaces, atmospheres, and temperature profiles were used during this Phase I effort. The most promising conditions included sintering in either vacuum or air atmosphere at a temperature of 1550°C for a period of two hours. Two temperature ramp rates were commonly used to reach 1550°C, either a 5 C/min ramp to 1550°C, or a 5C/min ramp to 1000°C, followed by a 2 C/min ramp to 1550°C. Domes were cooled at a rate of 2C/min to 3C/min without cracking.

#### **4.4 Hot Isostatic Pressing Conditions**

Hot Isostatic Pressing was performed using fresh argon gas and a molybdenum foil enclosure covering the domes. The temperature was increased at a rate of 3C/min to the final HIPing temperature of 1750C or 1850C. The pressure was also gradually increased to 30 ksi



concurrently with the temperature increase. All HIP cycles included a 5 hour hold at maximum temperature which was followed by a cooling rate of 2C/min to 3C/min.

## **5. Results and Discussion**

### **5.1 Preliminary Sintering Studies**

Since little was initially known about the sintering conditions required to produce transparent spinel, a series of tests were performed to investigate several sintering temperatures and show their effect on the resulting grain structure. Initial disk samples were pressed using powder from Baikowski lot 21834 powders were CIPed without binder, and sintered at temperatures of 1550°C, 1600°C, and 1650°C for 2 hours. These sintering trials revealed that 1550°C was the optimal maximum temperature for this powder batch. Optimal sintering conditions are known to vary with powder surface area and activity, making this a necessary test of the sintering behavior without incorporated binder. These trials produced an excellent series of samples with light transmission comparable to that produced by hot pressing samples. Several of these samples have been sent for testing by a third party, but one of these samples (sintered at 1600°C for two hours and HIPed at 1850°C) is shown below in Figure 3 as a representative sample.

Baikowski Powder Lot 21834  
Dry Milled – No Binder  
Sintered at 1600 C – 2 hours  
HIPed at 1850 C

---

**1 inch**

Figure 3: Polished pressureless sintered spinel sample following sintering at 1600°C and HIPing at 1850°C. This sample is approximately 3.5 mm thick.

All three samples appeared visually similar, but small microstructural differences were observed in the optical microscope, shown in Figure 4. Essentially, the main microstructural difference between these samples was the presence of pores trapped within some of the grains in the samples sintered at higher temperatures. Microstructural investigation of samples sintered at 1550°C showed almost no pores remained in the material following HIPing at 1850°C. Those pores that remained, although few, existed only at grain boundaries, not in the bulk of the grains. At higher sintering temperatures of 1600°C and 1650°C, it was clear that pores had been trapped and encapsulated within grains. At high temperatures, the grain boundary mobility can exceed pore mobility, causing the pore to be trapped in the bulk of the growing grain. Once pores

become trapped, they are very difficult to remove and act as internal scattering sites, lowering the overall transmitted wavefront for the spinel. The transmission through the material in the UV/VIS wavelengths was measurably degraded by the presence of these encapsulated pores, particularly in the sample sintered at 1650°C.

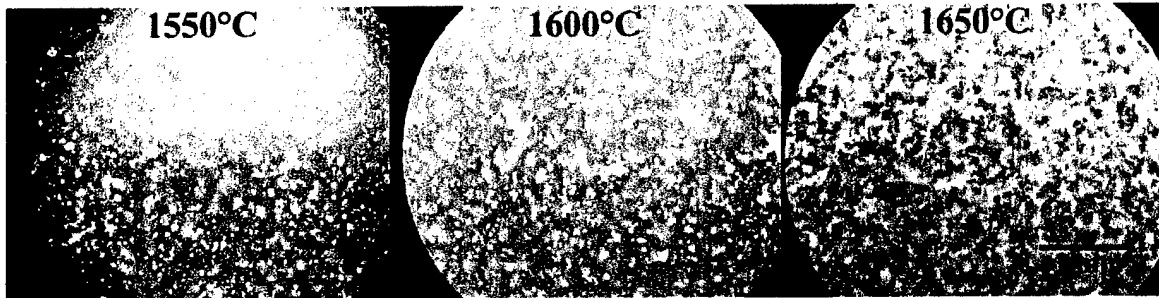


Figure 4: Microstructure comparison for pressureless sintered samples after HIPing at 1850°C. The sinter temperature is shown at the top of each picture, and each sample was held at its dwell temperature for 2 hours. The scale bar on the right is 1 mm. The optical transmission curves for these samples are shown below in Figure 5.

Transmission measurements were recorded by a spectrophotometer between 200 nm and 2250 nm by TA&T at the U.S. Army Research Laboratory. These curves are shown below for pressureless sintered (PS) samples in Figure 5 against the transmission curve for a hot pressed (HP) part, which have traditionally exhibited a higher transmission over the same wavelengths. Overall, sintering at 1550°C was found to produce optical transmission nearly as good as some of the best hot pressed parts produced at TA&T. Relative to the hot pressed samples, only a slight amount of transmission loss was observed in the optical range for the samples sintered at 1600°C and 1650°C, caused by the pore encapsulation described above. The full spectrum was measured through the mid-wave infrared regime, and is shown below in Figure 6. At a wavelength of 4.8 microns, the total transmission through the 3.5 mm thick sample was 80%.

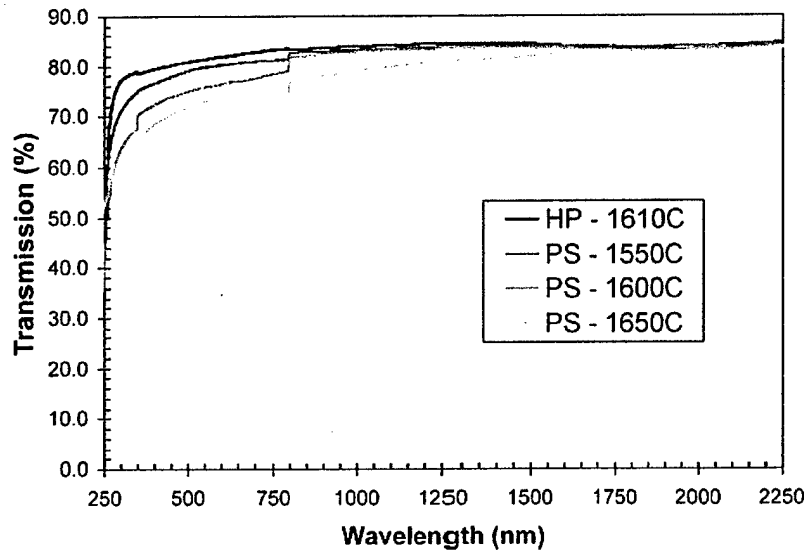


Figure 5: Light transmission curves measured as a function of wavelength for samples processed by hot pressing (HP) at 1610°C or pressureless sintering (PS) at temperatures of 1550°C, 1600°C, or 1650°C. All samples were HIPed at 1850°C for 5 hours following hot pressing or pressureless sintering.

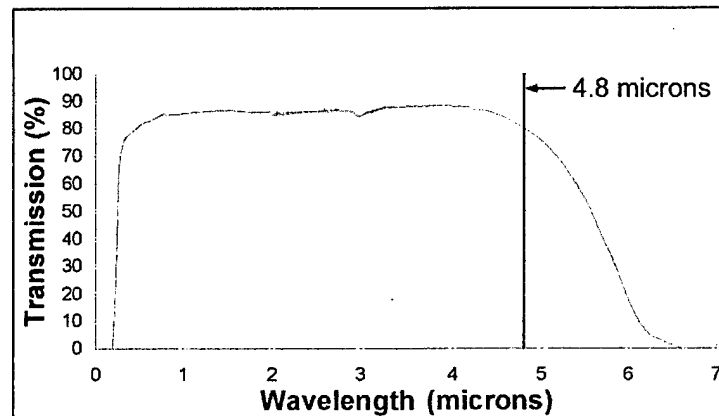


Figure 6: Full spectrum transmission curve through the mid-wavelength infrared region. This sample was sintered at 1550°C for 2 hours, and the polished thickness was 3.5 mm. At a wavelength of 4.8 microns, the transmission is 80%.

## 5.2 Testing of Binders and Sintering Aids

As dome size is increased, mechanical integrity of the CIPed green part becomes a greater concern. The part must endure handling as it is removed from the mandrel, which are then stored until ready for burnout, and transferred between burn-out and sintering furnaces. Binders used to increase green strength, as well as any sintering aids, must be completely removed during the burnout step. Binder remnants or sintering aids are often trapped in grain boundaries, creating scattering sights or macroscopic inclusions that degrade the transparency of the material. Coupon level experiments with different binder and sintering aid combinations

were conducted using selected sintering protocols. This coupon matrix is shown below in Table 1. Multiple samples of each powder composition were pressed. A variety of experimental compositions were tested according to the requirements of the workplan.

Table 1: Results summary of uniaxially pressed and CIPed 2.5 inch disks

Powder	Binder	wt % Binder	Sinter Aid	wt % Sinter Aid	Result After CIPing
Baikowski 21834	None		None		Edge Cracking
Baikowski 21834	PVA	2	None		Broken
Baikowski 21834	Oleic Acid	2	None		Good
Baikowski 21834	PEG	2	None		Good
Baikowski 21834	None		LiF	0.01	Good
Baikowski 21834	None		LiF	0.05	Good
Baikowski 21834	None		LiF	0.10	Good
Baikowski 21834	None		LiF	0.25	Good

Pressed spinel disks without binder had brittle edges that frequently chipped off, making this a non-ideal condition. Spinel powders milled with 2 wt% polyethylene glycol (PEG) or 2 wt% oleic acid produced structurally sound samples that did not experience chipping at the edges. Samples milled and uniaxially pressed with 2 wt% polyvinyl alcohol (PVA) remained structurally intact until CIPing was performed. During CIPing, every sample containing PVA broke into small fragments, shown in Figure 7. PVA was eliminated as a potential binder.

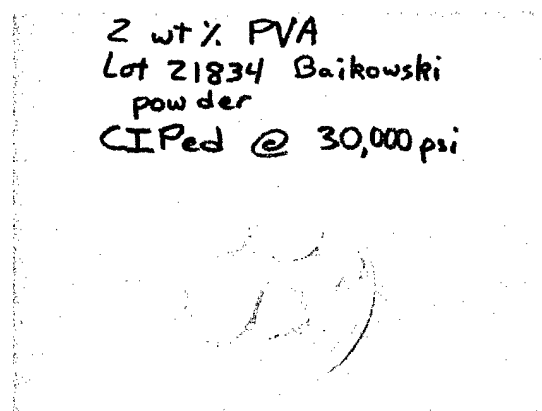
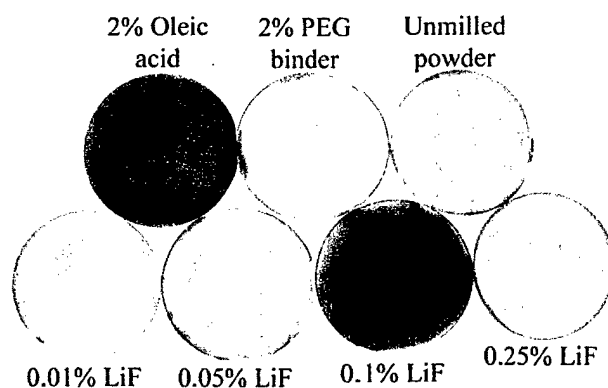


Figure 7: Sample containing Baikowski Lot 21834 powder and 2 wt% PVA CIPed at 30 ksi.

The two sintering profiles involved a two step ramp rate with a 2 hour hold at maximum temperatures of 1500°C and 1550°C, respectively. Favorable results were observed for samples sintered at 1550°. Previous sintering trials with holds at 1600°C and 1650°C were shown to result in pore entrapment, which were not completely removed in the HIP stage. Photographs of the HIPed coupons sintered at 1500°C and 1550°C are shown on a lightbox in Figures 8 and 9, respectively. White streaks are frequently observed on the surface of sintered-HIPed parts before polishing. The nature of the streaks is unclear, but they are not present in the bulk of the sample, and are removed during polishing. Samples formed from unmilled powder sintered at both temperatures showed excellent transparency in the unpolished state, and are anticipated to give transmission values near theoretical transmission values. Of the binder choices (PEG 4000 and Oleic Acid), PEG appears to be removed more easily, and produces better overall clarity than the oleic acid. Noticeable differences were observed in samples with LiF sintering aid between the two sintering temperatures. At the lower sintering temperature (1500°C), the LiF appears to have been completely removed, even in samples with 0.25 wt% LiF, leaving parts with a uniformly clear appearance (except the previously noted surface streaking). Samples with LiF additive sintered at 1550°C appeared to have sintered quickly, trapping the LiF, and leading to opacity in areas, and non-uniformity in clear regions. Overall, these sintered samples provide evidence that the sintering profile has not yet been optimized, and further improvements, such as a reduction of sintering temperature to 1500°C, may further help improve the quality of the sintered parts.



Sintering Profile: 5°C/min to 1000°C, 2°C/min to 1500°C,  
2 hour hold, 2°C/min to room temperature

Figure 8: Samples sintered at 1500°C using the binders, sintering aids, and profile indicated, and HIPed at 1850 for 5 hours. White streaks on the samples are representative of the appearance of disks in the unpolished state, and are only present on the surface of these samples.

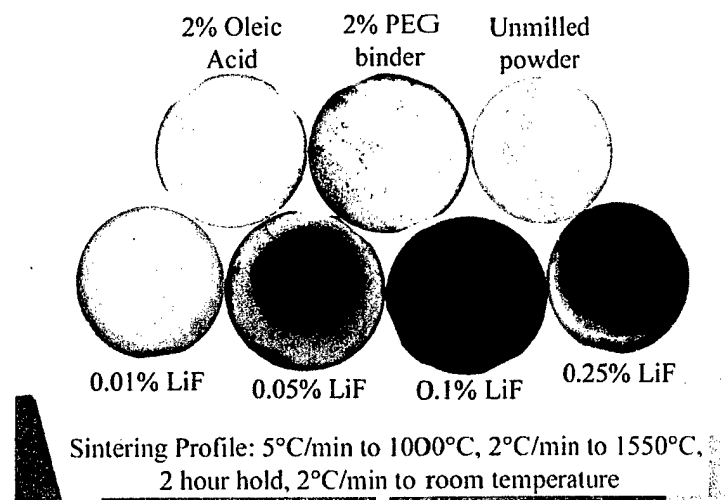


Figure 9: Samples sintered at 1550°C using the binders, sintering aids, and profile indicated, and HIPed at 1850 for 5 hours. White streaks on the samples are representative of the appearance of disks in the unpolished state, and are only present on the surface of these samples.

### 5.3 Development of CIPing techniques and protocols

Previous dome development work performed by others suggested that isostatically pressing the initial dome form onto a mandrel at 30 ksi, followed by a second isostatic pressing step at 60 ksi produced finished domes with optimal strength. This two-step CIPing protocol was used initially on 3.5 inch diameter domes. The first step involved pressing at 15 ksi on a mandrel, and then rebagging in a latex balloon and re-CIPing the dome separately at 30 ksi. In addition, several domes were individually CIPed only once at total isostatic pressures of 15 and 30 ksi. The mandrel and polyurethane mold that form the die cavity are shown in Figure 10 during various stages of the mold filling process. The various CIP protocols for pressing 3.5 inch domes with both dry milled and spray dried Baikowski Lot 21834 powder is presented in Table 2. Spray dried powder is agglomerated by simultaneously spraying and drying an emulsion of powder. The exact details of the processing of this powder are a proprietary development of the powder supplier. However, the powder flows and packs more easily, and generally produces parts of a higher green density. Some of the domes pressed using the conditions in Table 2 are shown below in Figure 11. Significant advances occurred in the mold sealing and filling process steps during the CIPing study. These steps were easily adaptable for sealing and filling the larger 7 inch dome molds.

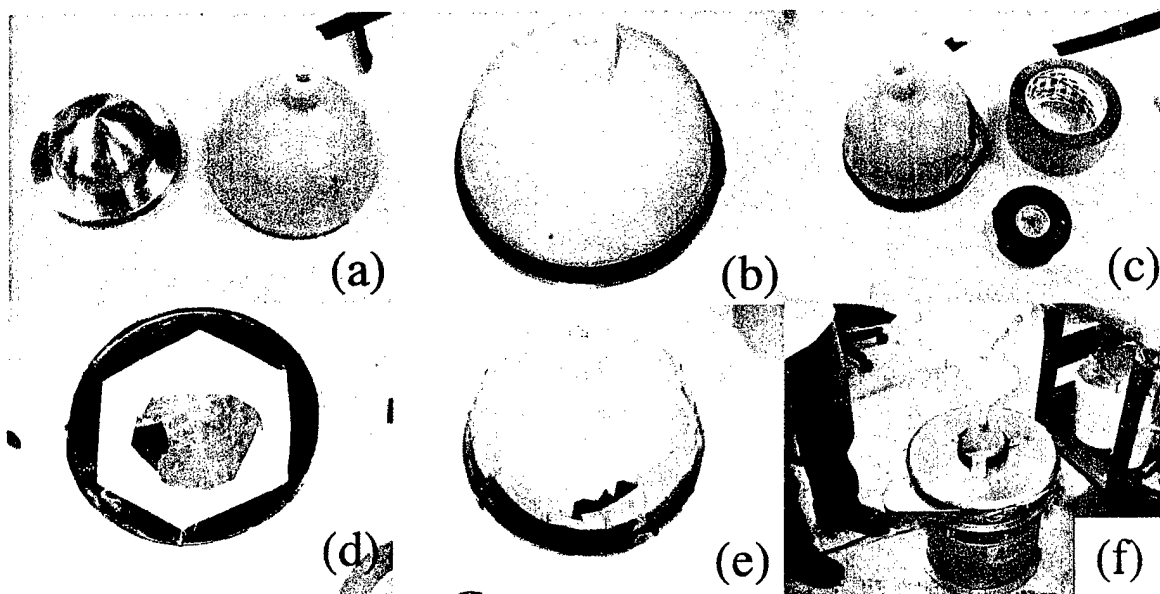


Figure 10: Stages in cold isostatic pressing of domes; (a) Mandrel and polyurethane cover (shown separately) were sealed together to form the dome cavity; (b) An elastic band was applied to the polyurethane mold to compress it onto the mandrel; (c) Duct tape and vinyl electrical tape were applied to the mold/mandrel couple to seal against water pressure; (d) Bottom of the fully taped mandrel; (e) the sealed mold; (f) Vibratory table accelerated loading of powder into the mold cavity.

Table 2: List of 3.5 inch diameter domes CIPed by TA&T at the Army Research Laboratory

Powder <sup>a</sup>	1 <sup>st</sup> CIP Pressure (ksi) Mandrel	2 <sup>nd</sup> CIP Pressure (ksi) Without Mandrel	CIP Treatment Designation
Ceralox Powder	30	n/a	A
Dry Milled 21834 <sup>*</sup>	15	n/a	B
Dry Milled 21834 <sup>**</sup>	15	30	C
Dry Milled 21834 <sup>€</sup>	30	n/a	A
Spray Dried 21834	15	n/a	B
Spray Dried 21834	15	30	C
<b>Spray Dried 21834 (Best Overall Condition)</b>	<b>30</b>	<b>n/a</b>	<b>A</b>

<sup>a</sup> All samples are made from Baikowski lot powders as indicated, except the first sample

<sup>\*</sup> These samples cracked during annealing at 1550°C

<sup>\*\*</sup> This sample cracked severely during sintering at 1550°C

<sup>€</sup> These samples did not survive the CIP process

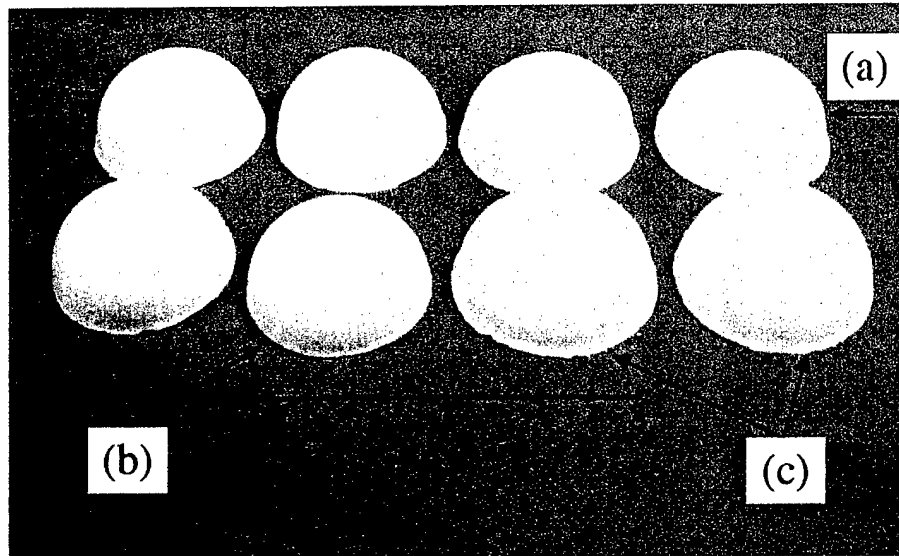


Figure 11: Green pressed domes formed using the CIP at the Rodman Materials Laboratory of the Army Research Laboratory; (a) Spray Dried Baikowski 21834 Powder CIPed at 30 ksi on a mandrel; (b) Spray Dried Baikowski 21834 Powder CIPed at 15 ksi on a mandrel and reCIPed at 30 ksi in a rubber balloon; (c) Spray Dried Baikowski 21834 Powder CIPed at 15 ksi on a mandrel.

#### 5.4 Sintering of Development Domes

Since the starting powder has a dramatic effect on the sintering behavior and resulting quality, development of sintering protocols and trials is best divided into trials performed using each powder.

##### 5.4.1 Sintering of Domes Formed From Ceralox Powder

Several 3.5 inch domes were sintered using various burnout and sintering profiles. One dome formed from Ceralox powder was sintered at 1600°C for 2 hours and HIPed at ARL at 1850°C. This dome is shown below in Figure 12. Unfortunately, Ceralox powder has been found to have critical, currently unidentified, impurities that caused it to remain opaque during sintering and HIPing. Since the processing and handling procedures for the powders are the same as those used for the Baikowski Lot 21834 powder, the problems are likely inherent in the Ceralox powder. This unknown impurity is not present in the powder as a distinguishable second phase or as specks in the starting powder.



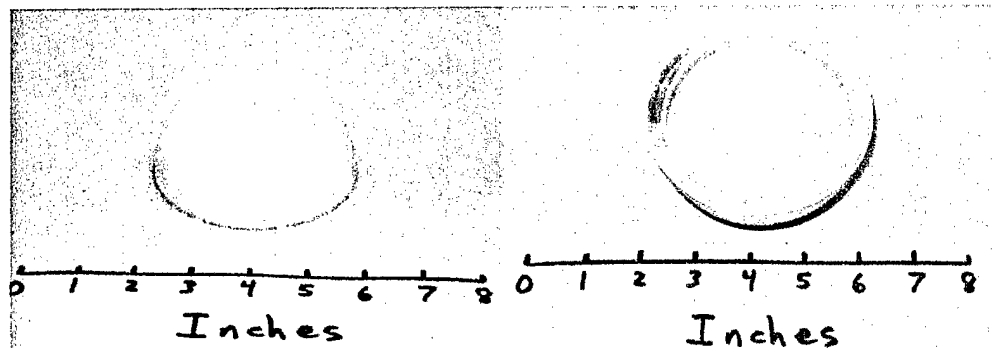


Figure 12: Ceralox dome CIPed at 30 ksi, sintered at 1600°C for 2 hours, and HIPed by the Army Research Laboratory at 1850°C.

#### 5.4.2 Sintering of Domes Formed From Dry Milled Baikowski Lot 21834 Powder

Initial dome development was performed using dry milled Baikowski Lot 21834 powder and 3.5 inch diameter dome die. Domes pressed at a CIP pressure of 30 ksi with graphite spray die lubricant cracked repeatedly, so domes were pressed at a lower CIP pressure of 15 ksi, and a variety of release agents were simultaneously tested. These domes remained intact, but developed hairline cracks during the sintering process. The sintered domes are shown below in Figure 13. These domes were CIPed and sintered before spray dried powder was received at TA&T.

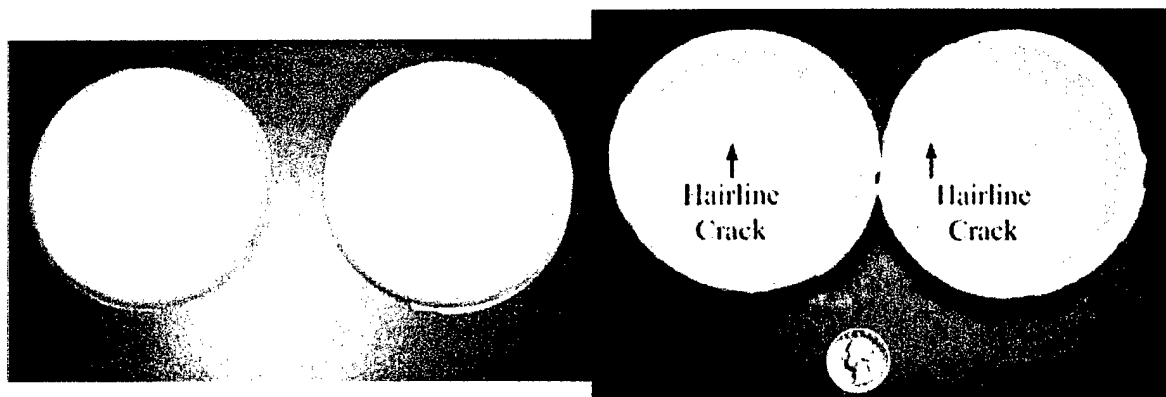


Figure 13: Domes sintered at 1550°C for two hours in air atmosphere. Both domes were formed from milled Baikowski Lot 21834 powder isostatically pressed at 15 ksi.

#### 5.4.3 Sintering of Domes Formed From Spray Dried Baikowski Lot 21834 Powder

Since each powder CIPed differently, different CIPing protocols were also investigated concurrently with sintering trials on domes formed using spray dried Baikowski Lot 21834 powder. Initially, the two-step CIPing cycle and a sintering schedule similar to a previous dome study was evaluated. The dome was CIPed on a mandrel to a pressure of 15 ksi, and then reCIPed in a latex balloon at a pressure of 30 ksi. This CIP cycle was referred to as CIP cycle C.

A simple sintering cycle was then performed on two domes by heating at a rate of 5°C/min to 1550°C, holding for 2 hours, and cooling at a rate of 2°C to room temperature. All domes sintered using this two-step CIP cycle experienced some type of cracking, severe cracking, or warpage. Examples are shown below in Figure 14.

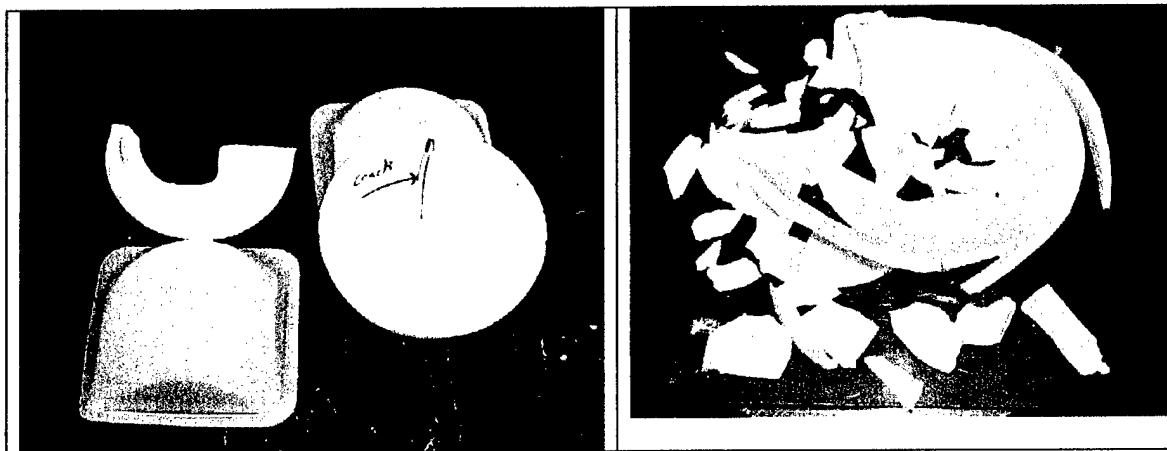


Figure 14: Domes formed from spray dried Baikowski Lot 21834 powder CIPed at 15 ksi on a mandrel, reCIPed at 30 ksi in a latex balloon, and sintered at 1550°C for 2 hours. All experienced cracking and warpage.

Domes pressed using a single CIP cycle to 15 ksi (CIP cycle B) also experienced cracking, although the warpage observed in the sintered part was not as severe as the damage in domes that were subjected to the two step CIP cycle. One of these domes is shown in Figure 15.



Figure 15: Sintered formed from spray dried Baikowski Lot 21834 powder CIPed at 15 ksi on a mandrel and sintered at 1550°C for 2 hours.

CIPing at 30 ksi, followed by sintering at 1550°C yielded transparent domes (after HIPing), with no cracks. This CIPing-sintering combination became the standard protocol for all future dome fabrication. The first of these domes is shown below in Figure 16, which achieved 98.1% density during the air sintering stage. The dome burnout protocol involved heating at 1°C/min in air to 700°C, holding at 700°C for 4 hours, and cooling at a rate of 2°C/min. Sintering was performed by heating at 5°C/min to 1550°C, holding for two hours, and cooling at 2°C/min to room temperature. Crossed polarizers show some degree of density variation, apparent in Figure 15, by the dark region near the apex of the dome. Overall the dome was structurally sound and served as a significant advancement towards the goal of transparent spinel domes. Subsequent HIPing revealed that some small inclusions remained in the dome. Longer burnout schedules aided in producing more transparent domes. One of these domes is shown in Figure 17.

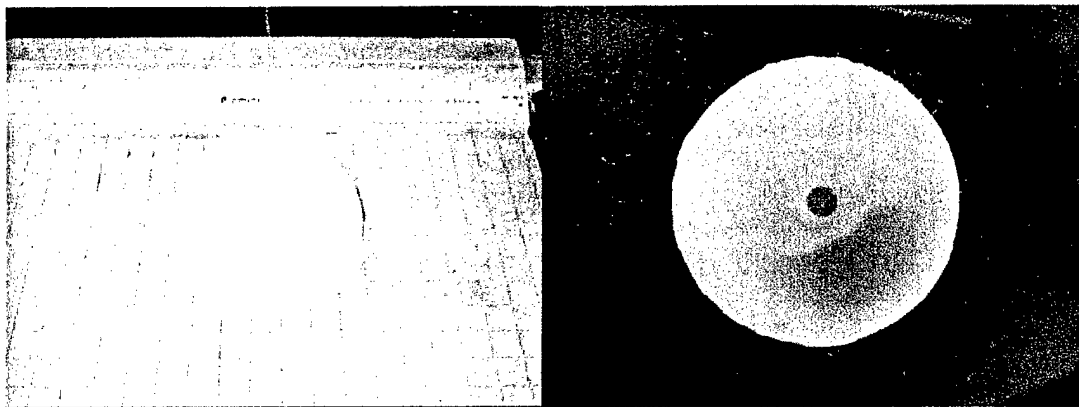


Figure 16: The first fully intact, sintered 3.5 inch diameter dome, produced at TA&T on 15 March, 2004. (Left) View of the outer surface of the dome; (Right) View of the same dome placed on a lightbox between crossed polarizers to show qualitatively areas of residual stress within the part. The dark circle in the center of the part is a result of the powder filling process in the CIP die, and would be removed in actual production of this dome. This dome was fabricated by CIPing spray dried Baikowski Lot 21834 powder at 30 ksi and sintering at 1550°C for two hours in air atmosphere.

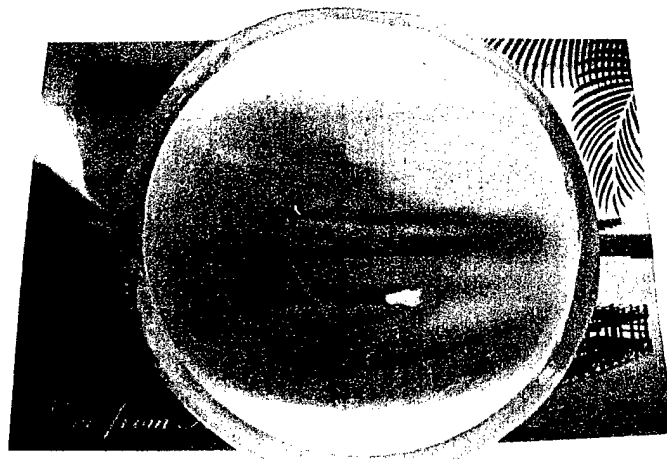


Figure 17: One of the transparent domes fabricated by CIPing spray dried Baikowski Lot 21834 powder at 30 ksi and sintering at 1550°C for two hours in air atmosphere. This dome is shown after HIPing at 1850 for 5 hours. Many of the small black inclusions evident in this dome have been eliminated in subsequent domes by improved burnout schedules.

#### 5.5 Scale-Up to Fabrication of 7 inch domes

The 7 inch molds (shown below in Figure 18) were received during the week of 17 March, and were immediately integrated into the development program. Using many of the established protocols from the 3.5 inch diameter developmental domes, development work began on the 7 inch domes using the spray dried Baikowski Lot 21834 powder. One of the first 7 inch diameter green domes is shown below in Figure 19.

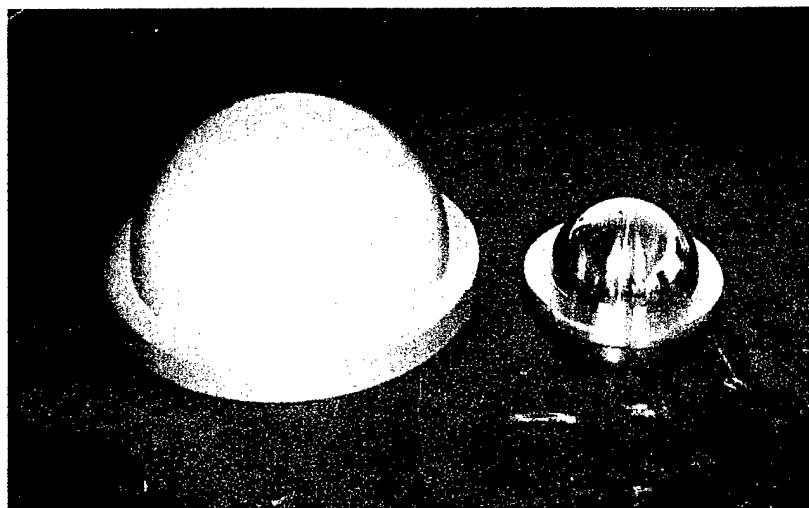


Figure 18: (Left) 7 inch cold isostatic press mold mandrel for fabrication of Joint Common Missile domes; (Right) 3.5 inch developmental cold isostatic press mold mandrel for fabrication of stinger missile domes.

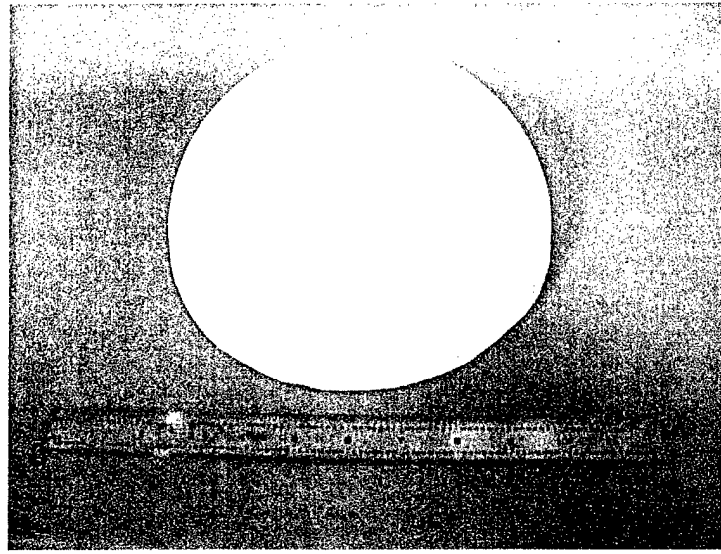


Figure 19: Green pressed 7 inch diameter dome formed from spray dried Baikowski Lot 21834 powder CIPed at 30 ksi on aluminum mandrel.

During concurrent development of the CIP process and sintering protocols, a high density of cracks were observed along the outer edge of the 3.5 inch diameter domes. At this edge, a non-uniform stress was placed on the green dome due to mold constraints and the joint between the CIP bag and the metal mandrel. A grinding step was implemented to polish the edges of all 7 inch domes, providing a smoother surface and eliminating stress concentrators that caused cracking during sintering. A finished edge is shown in Figure 20 for one of these 7 inch green domes. This treatment completely eliminated subsequent cracking in the 7 inch domes. Future dome designs will incorporate additional material on this edge to compensate for the edge removed during the grinding step.

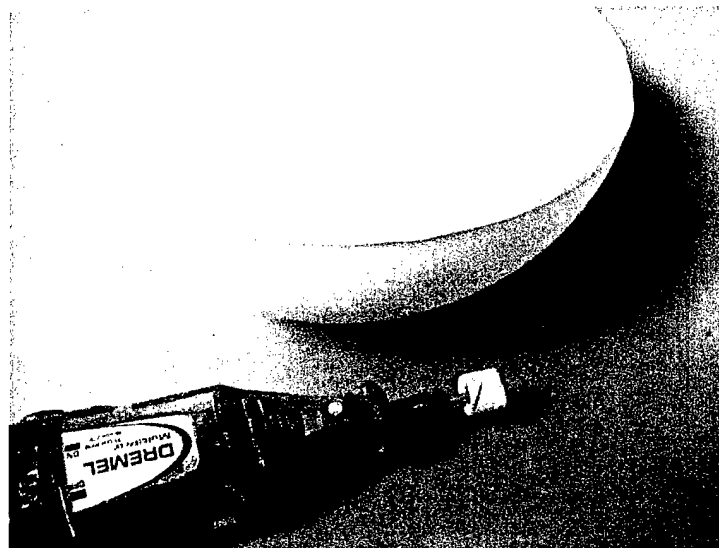


Figure 20: Ground edge of a green dome formed by CIPing spray dried Baikowski Lot 21834 powder at 30 ksi on a mandrel. Grinding the edge completely eliminated edge cracking.

Several of these 7 inch diameter domes have now been sintered in air using sintering profiles similar to that originally used for the 3.5 inch domes. The burnout hold time was increased to 8 hours at approximately 700°C. Additional time beyond 8 hours at 700°C does not appear to improve the overall clarity of the dome. After the burnout was completed, domes were subsequently heated to 1000°C at 5°C/min, then to 1550°C at 2°C/min to 3°C/min, held for 2 hours at 1550°C, and cooled at about 2°C/min. HIPing was performed after the sintering treatment. After a number of successful air sintered 7" domes were fabricated, it was decided that similar sintering protocols in vacuum should be explored.

### 5.6 Vacuum Sintering Domes

While sintering in air (and subsequent HIPing in argon) produced dramatic results, several sintering cycles were performed under vacuum after the required binder burnout in air. Using a similar sintering cycle, the 7 inch dome shown below in Figure 21 (left image) was sintered in vacuum at the Army Research Laboratory. Following the prescribed burnout schedule, performed in air, sintering of this dome was accomplished by heating in vacuum to 1550°C at a rate of 3°C/min, holding for 1 hour at 1550°C, and cooling at a rate of 2 to 3°C/min. It is shown next to the air-sintered dome in Figure 21 for comparison. The burnout and sintering schedules are shown graphically below in Figure 22.

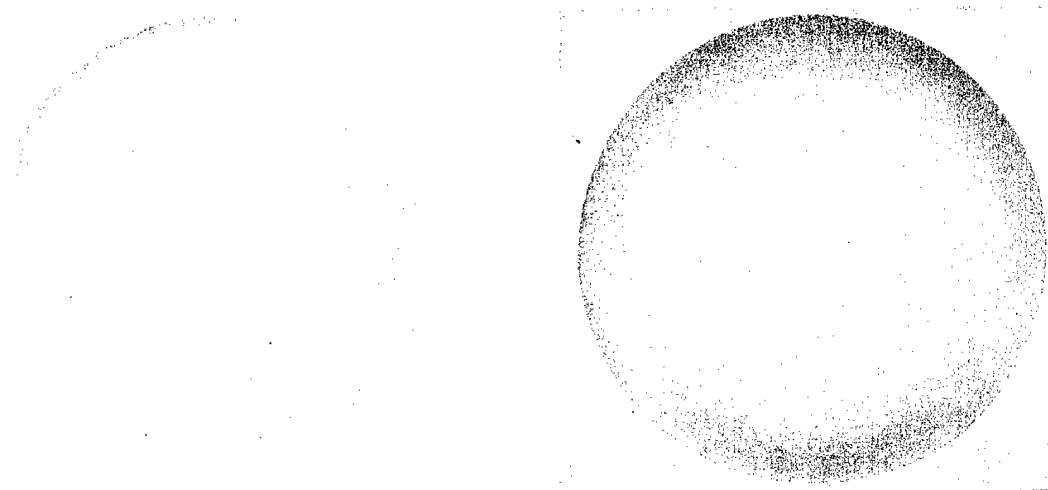


Figure 21: (Left) Transparent 7 inch diameter dome produced by vacuum sintering. (Right) For comparison, an air-sintered dome is also shown. The vacuum sintered dome was lighter in color, slightly more transparent in the unpolished state, and appeared to have fewer embedded speckles. After polishing, it will be compared directly with the polished dome produced by air sintering. The sintering profile for the vacuum sintered dome is shown in Figure 22.

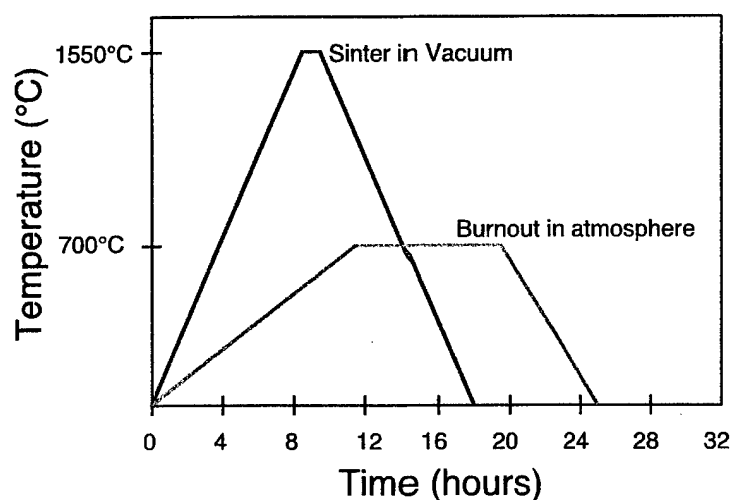


Figure 22: Sintering and binder burnout profiles for domes sintered in vacuum at the Army Research Laboratory.

There is a region of slight discoloration in the center of the vacuum sintered dome, indicating a reaction with the grafoil spacer on which it was placed. The same problem did not occur in air sintering because grafoil was not used. A different support material will be used to avoid this problem on subsequent runs. Qualitatively, the transparency of the vacuum sintered dome in the unpolished state appears to be superior (outside the contaminated region) to that of the air sintered dome shown in Figure 21. Given that sintering atmosphere has proven to be an

important factor, it is one of the test variables to be explored in more detail in the proposed Phase II effort.

The main issue affecting further development of these spinel domes is the origin and nature of remnant speckles found in the HIPed blanks due to a processing condition present in the as-received raw materials. Many of these speckles could be observed even in the unpolished state. The specific nature of the speckles is likely attributed to undissolved organic binders used in the spray drying process, which after the sintering procedure leaves voids on the order of the size of the undissolved particle. The void space, being much larger than the average void space between spinel particles would lead to non-uniform shrinkage during sintering and densification. The subsequent effect would be to leave residual porosity or even small cracks in the microstructure. These would act as large scattering sites and presumably degrade the mechanical properties of the dome. The elimination of these voids is the remaining hurdle confronting the production of JCM-ready, transparent spinel domes. To this end, TA&T is working closely with the raw material supplier to eliminate the cause of these visible impurities. Despite the persistence of these speckles, the current transparent spinel dome production process is very stable and repeatable.

Sample material from the vacuum sintered dome will be polished for comparison with the air-sintered dome. Although vacuum sintering does not add significant cost, air sintering is preferred because it is the more robust and forgiving process with regard to removing organic based impurities (hair, dust, lint, etc) as a normal part of the process. Additionally, air sintering provides a modicum of time and thus cost savings over vacuum sintering because both binder burnout and sintering can be conducted in the same processing run. Vacuum sintering would require an additional step and associated cost in transferring domes from the binder burn-out furnace to the vacuum sintering furnace. The small additional costs of vacuum sintering, if deemed necessary, would be almost of no consequence in the overall delivered dome price for the JCM contract compared with the other aspects of dome production such as polishing, EMI gridding, or skirt attachment.

## **6. Future Objectives**

In the Phase I effort, the factors that affect integrity of the green part, and sintering profiles that produce a high degree of optical clarity have been identified. This knowledge will be brought to bear in advancing the dome fabrication process in the Phase II effort, encompassing the following objectives:

### **Objective 1: Analysis of the spray dried powder, and refinement of procedures for removal of binder and organics used in the spray drying process**

Despite the nearly transparent appearance of the most recent group of 7 inch domes produced by pressureless sintering, small inclusions or agglomerates still remain in many of the TA&T domes. Removal of these agglomerates, or creating spray drying processing routes that avoid agglomeration, will be one of the main objectives of the Phase II program. These processing improvements will bring the optical quality of the domes to the level required for commercial production.



## **Objective 2: Refinement of the sintering process for spinel by performing a comprehensive study of microstructure development during sintering**

A working knowledge of the processing window has been established for producing optically transparent spinel. However, this process has not been optimized, and further test conditions, as well as analytical observation of the sintering cycle using a dilatometer, is required in order to optimize this process. Currently, there is a poor understanding of the competing processes of surface and bulk diffusion through the sintering cycle. Without full understanding of this behavior, producing a material with the lowest possible density of scattering sites and the smallest grain size will be impossible. In addition, the possibility of sintering directly to transparency and eliminating the HIP cycle is still under investigation, but it is unlikely without further process optimization.

## **Objective 3: Refinement of the HIPing process to determine overall optimal sample processing conditions**

Since the HIPing process is typically performed at a temperature several hundred degrees higher than the sintering process and held at that temperature for a longer time, the HIP process is the determining step in the resulting grain size of the pressureless sintered sample. Since strength is inversely related to grain size, there is significant interest in minimizing the grain size in the finished dome material. By performing a comprehensive study of HIP conditions and the resulting grain sizes produced, the most optimal HIP conditions for producing fine-grained transparent spinel will be determined.

## **Objective 4: Exploration nanoscale methods to inhibit excessive grain growth**

In addition to minimizing the HIP conditions, grain boundary pinning is another strategy for minimizing average grain size and preventing exaggerated grain growth. Very small insoluble particulate second phases can be introduced into the spinel powder prior to sintering to inhibit grain growth. If grain boundary pinning particulates are small enough, typically nanoscale, they will not affect the optical transmission of the part, and may therefore be used to inhibit exaggerated grain growth. Prior work with spinel suggests that cerium oxide may be one potential candidate to pin grain boundary movement during sintering. Other candidate materials include silicon carbide.

## **Objective 5: Determination of fundamental optical, strength, and materials properties of TA&T spinel**

The properties of any material are dependent on their microstructure, and spinel is certainly no exception. While many of the properties and characteristics of spinel have been measured previously, they may have had dramatically different grain sizes or impurity levels. In order to design with the materials characteristics of TA&T's optical grade spinel, these fundamental properties must be measured for this material. These properties include a wide range of materials properties, including measurement of the resistance of the material to sand and rain erosion.

## **Objective 6: Work with coating companies to develop glass coatings for spinel**

Finishing and polishing of spinel is one of the most significant costs in producing spinel optical components. If this cost can be reduced by application of refractive index-matched glass, then spinel is even more attractive as an infrared transmitting optical window and dome material. Due to the considerable cost savings potential in polishing of spinel materials, TA&T will work with coating companies to develop these refractive index-matched glasses. Several companies are currently working on these coatings, and assisting them by providing coupon scale product or small dome shapes may expedite their efforts and success.

## **Objective 7: Homogeneity testing, Microstructure analysis, and strength testing domes and coupons**

Homogeneity and quality control will become significant issues given the dramatic number of domes that are anticipated in the Joint Common Missile Program. In order to ensure that domes produced during production meet the specifications given by the manufacturer, and to ensure that quality remains an ongoing focus of our investigation, methods for testing and quantifying the quality of 7 inch domes will be implemented.

## **7. Future Work**

### **Task 1: Powder Development and Testing**

Historically, early spinel powder lots from major powder suppliers have commonly had a variety of problems with powder purity and various contaminants detrimental to the optical quality of dense sintered materials. TA&T has worked closely with these companies to analyze powders, identify the nature and origin of chemical impurities, and refine production of spinel raw materials in order to meet our processing requirements. Phase I results have indicated that these problems can be compounded when organic additives are used in the formulation of the spray dried powder. Commercial spray dried powders are formed from the spinel raw material combined with proprietary mixtures of binders and dispersants into a liquid "slurry" that is sprayed into a large enclosed chamber. The organics that comprise the slurry and end up as binders in the spray dried powder can themselves be sources of contamination from their own innate chemical purity. Furthermore, the way in which the organic materials are dispersed into the powder may play an important role in the quality of the final sintered dome.

In addition to the numerous problems in removing the binder during the burnout stage, white flecks or inclusions have also been observed in many finished domes, and now appear to be the main defect in domes fabricated from Baikowski spray dried powder. The reason for the presence of these inclusions has already been discussed in the experimental results portion of this proposal. However, in general, it appears that agglomeration and trapping of pores during the spray drying process causes these flecks. Additional work will be completed through the tasks shown below to destroy these agglomerates and the resulting opaque inclusions in the final product.

The overall objective of this task is fourfold; First, to modify the spray dried powder processing conditions to remove and/or limit the formation of hard agglomerates within the spray

dried powder; Second, to fabricate domes using PEG binder as an alternative to the spray dried powder; Third, to determine atmospheres and temperatures that result in most complete binder removal; Fourth, to affect change in the spray drying process to avoid agglomeration that is believed to be the cause of white inclusions in finished domes.

#### **Subtask 1.1: (TA&T) Reduction of Spray Dried Powder Binder Concentration and Destruction of Agglomerates in the Spray Dried Powder**

Hard agglomerates and inclusions are thought to be due either to the incomplete removal of binder in the spray dried powder or agglomeration of powder particles into highly porous regions that do not sinter well and act as sinks for additional porosity within the microstructure during sintering. These subtasks are designed to test various strategies for removing or eliminating these inclusions through reductions of binder in spray dried powder, processing variations, or milling of the spray dried powder.

##### *Subtask 1.1.1: Reduction of Spray Dried Binder Load*

First, TA&T will work with Baikowski, International to examine the purity of the organics used to formulate spray dried powders to whatever extent is possible within their proprietary framework. If purity appears to be an issue, suitable higher purity replacement additives will be identified and new test batches will be produced. The resulting powder will be tested at the coupon level by fabricating 5 samples to be sintered under the best-known conditions. Second, another batch of spray dried powder containing less of the additives normally found will be produced. Reduction of the spray dried additives will decrease the flowability and tap density of the powder. However, these properties may also result in a relaxed binder burnout schedule, and may result in overall clarity improvements in the finished part. Specifically, TA&T will have two additional lots of spray dried formulated. The first lot of 50 kg will contain 1/2 the normal binder content. The second lot of 50 kg will contain 1/4 the normal binder content. A comprehensive binder burnout study will then be performed by pressing five, 3.5 inch diameter domes from each of these two additional lots of powder and five, 3.5 inch diameter domes from the original spray dried powder with normal binder load, a total of 15 domes with three different spray dried binder loads. One dome from each powder lot will be subjected to the same binder removal stage, under conditions to be determined in Subtask 1.3. However, these binder removal treatments are anticipated to be performed at 650°C or 700°C for periods of 4 to 48 hours, resulting in a comprehensive binder removal study and determination of conditions that result in the most complete degree of binder removal.

##### *Subtask 1.1.2: Spray Dried Processing Variations to Reduce Agglomeration*

Secondly, TA&T will subcontract to have another 50 kg lot fabricated by Baikowski whereby the initial spinel raw material received extended milling and filtering to break up and remove hard agglomerates. An additional five, 3.5 inch diameter domes will be fabricated from this third powder lot for inclusion in the binder removal study. Several full hemispherical 7" domes will be fabricated from whichever spray dried powder appears to give the best results.

#### **Subtask 1.2: (TA&T) Polyethylene Glycol as an Alternative Binder**

In addition to experimental work to determine the optimal binder load for producing spray dried powders, an alternative study will be performed with polyethylene glycol (PEG, molecular weight = 4000). The binder will be mixed with the power by ball milling instead of

spray drying. In coupon level studies during the phase I effort, PEG was determined to be the most promising binder in the matrix study, and this investigation will be continued with 3.5 inch diameter domes. Concomitantly with the binder burnout studies performed above, five, 3.5 inch diameter domes will be also be fabricated with 2%, ultra high purity PEG 4000 binder and included in the binder removal study.

### **Subtask 1.3 (TA&T) Thermal Gravimetric Analysis (TGA) of Starting Powder**

All lots of powder from Baikowski, International will be tested using a thermal-gravimetric analyzer (TGA) to determine the change in weight of a given powder samples as a function of temperature, including the powder with PEG 4000 binder. Temperatures at which dramatic mass loss and volatile removal are observed will form the basis for refinement of the burnout schedule. Extended hold periods will be put into place at these temperatures to improve volatile removal and oxidation of the carbonaceous residue. To that end, the choice of atmosphere during the binder removal stage is an important factor in improving the efficiency and effectiveness of the burnout process, and two atmospheres will be tested using a thermal gravimetric analysis system to observe mass loss with time. Determination of the cost effectiveness of oxygen gas use, as well as the installation of oxygen gas lines and storage facilities, will be accomplished by comparison of the overall time required to complete binder removal in air and oxygen atmospheres using the TGA.

#### *Subtask 1.3.1: TGA in Oxygen*

Use of an oxygen atmosphere during the burnout process may provide a number of potential benefits. If the overall burnout time can be reduced by improving the rate at which carbonaceous residues oxidize, the result will be greater throughput and reduced energy usage. The three spray dried powders proposed in Section 1.1 and the powder containing 2% PEG 4000 proposed in Section 1.2 will be tested in oxygen atmosphere using the TGA to determine the minimum time required for complete binder removal.

#### *Subtask 1.3.2: TGA in air*

The complication of installation of facilities to provide an oxygen atmosphere during binder removal favors processing in air. For comparison, the four powders proposed will be tested using the TGA while exposed to air, giving the overall time to complete binder removal in both air and oxygen atmospheres.

## **Task 2: Sintering Studies**

### **Subtask 2.1: Thermal Linear Analysis (dilatometer)**

The Thermal Linear Analyzer, or dilatometer, determines the expansion and/or contraction characteristics of a specimen as a function of temperature. Numerical and graphical results show the percent of linear thermal change (expansion or shrinkage) versus temperature using the dilatometer. Since packing characteristics of the green compact may be affected by spray dried binder content, at least one spray dried powder compact and one unmilled 1834 compact will be fabricated for testing in each atmosphere.

#### *Subtask 2.1.1: Dilatometer in air*

As with the binder removal procedures described above, performing the sintering of domes in air is the ideal, least complicated option. Two compacts (one formed from unmilled powder, one spray dried powder) will be formed to the requirements of the dilatometer system and tested to determine densification characteristics as a function of temperature and time. Initial dilatometer runs will be based on the best known sintering profile at the time. Subsequent tests will be combined with grain size analysis to optimize the sintering rate in the intermediate and final stage of sintering, similar to previous work performed by RCS, Inc.

#### *Subtask 2.1.2: Dilatometer in oxygen*

The presence of excess oxygen during sintering will facilitate the removal of any residual organic impurities and inclusions and also to eliminate the reducing effect by other gasses in the sample chamber during firing or by the impurities themselves. To test the benefit and feasibility of sintering in oxygen, three dilatometer tests will be performed using compacts similar to those in Subtask 2.1.1. One will be a repeat of the best results in air, and the others will be using a sintering profile that get progressively shorter in time overall. Lower sintering temperatures and shorter times translate to lower cost components.

### **Task 3: HIPing studies**

In order to determine the overall optimum HIP processing parameters, it is necessary to consider temperature, hold time at elevated temperature, and pressure, as well as the variety of possible starting conditions of the sintered material. Grain growth behavior is strongly dependent on temperature because the atomic mechanisms controlling grain growth have the same dependency. There exists a regime inherent to any given material in which the grain growth process or rate of growth becomes very rapid and even uncontrolled. The end result is a substantial increase in the mean grain size and/or the development of a bi-modal distribution of grain sizes. In either case, the end result leads to limits on the strength of a sintered part and more subtly could have other indirect effects in areas like grinding and polishing. Near the critical transition region, which for transparent spinel is around 1650C, small temperature differences are anticipated to show large differences in overall HIPing behavior. In contrast to the standard sintering cycle, the HIP cycles that were found to be most beneficial use soak temperatures between 1650°C to 1850°C for times up to 15 hours. As these temperatures are above the critical rate for grain growth, the HIP cycle becomes the determining factor for final grain size in sintered spinel. The objective of our HIP study will be to minimize the time necessary for HIPing above 1650C or conversely, reduce the HIP temperature below 1650C. At temperatures below 1650C, the time factor in grain growth will not be as strong and that becomes increasingly true the farther one gets below 1650C. A schematic of the general nature of the HIP processing window for pressureless sintered parts is shown schematically in Figure 23. The conditions typically used are shown with dots.

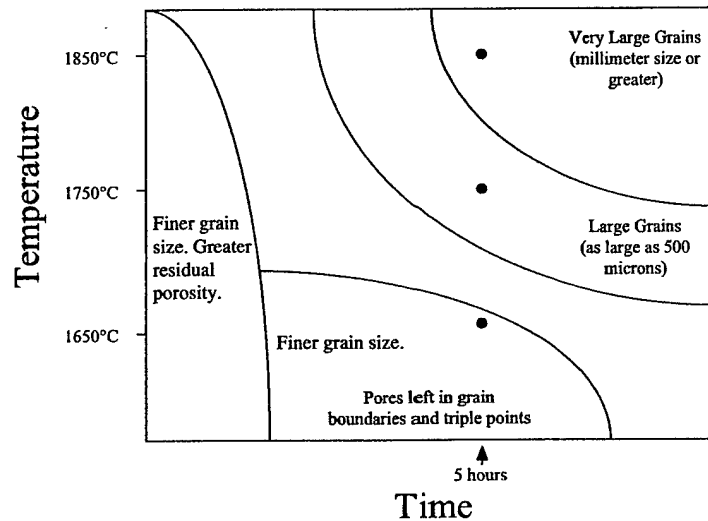


Figure 23: Schematic representation of the current understanding of the processing window for HIPing of spinel parts produced by pressureless sintering.

A matrix of processing conditions will be investigated using samples sintered under the best protocol tested in the Phase I effort, a 5°C/min ramp to room temperature, a 2 hour hold at 1550°C, and a 5°C/min ramp back to room temperature. This sintering condition was determined to be the ideal sintering condition ( $\pm 50^\circ\text{C}$ ) in the Phase I effort, and the rate of grain growth is not sufficient to trap pores in growing grains. At least 13 coupon-size samples will be sintered using this schedule from both the spray dried powder and unmilled Baikowski powders. In addition, samples will be sintered to lower temperatures (below 1550°C) or higher temperatures (up to 1650°C) for shorter times including a no-hold condition. The no-hold condition would be a simple ramp up and then ramp down. The acceptance/rejection criteria for these samples will be the density of the sintered part. Parts with densities around 93% and higher will be considered for HIPing as they are likely to have closed porosity and will be capable of being acted upon by the HIP. Any part below 93% theoretical density will not be suitable for HIPing and will be rejected from this portion of the study.

### Subtask 3.1: Matrix of Processing conditions

Of the many samples that are to be processed in this Task, they are to be HIPed using the conditions shown below in Table 3. This will provide a comprehensive assessment of the microstructures produced under the various processing conditions.

Table 3: Possible Matrix of HIP conditions<sup>§</sup>

Temperature (°C)	Pressure (ksi)	Duration (hrs)	Sintered Temp./Time
1450	30	5	1550/2h
1450	30	10	1550/2h
1450	30	20	1550/2h
1450	30	48	1550/2h
1550	30	5	1450/2h
1550	30	10	1450/2h
1550	30	20	1450/2h
1650	30	5	1650/0h
1650	30	10	1650/0h
1650	30	20	1650/0h
1750	30	5	1550/2h
1750	30	10	1550/2h
1750	30	20	1550/2h
1650	30	5	1550/2h
1650	30	10	1550/2h
1650	30	20	1550/2h
1750	10	10	1550/2h

<sup>§</sup> - These choices depend on actual sintered density and may have to be modified based on the 93% criteria.

### Subtask 3.2: Transmission Spectrum from Selected Samples

Quantitative measurement of the ultraviolet and visible transmission spectrum from each sample fabricated above in Subtask 3.1 will show how general processing trends affect transmission characteristics. A general trend towards opacity is anticipated for lower temperatures and shorter times as a result of incomplete removal of pores from the grain boundaries by grain growth. A general trend towards enlarged grains is anticipated at higher temperatures and longer times.

### Task 4: Post-HIP Annealing Treatments

Incorporation of contaminants from the chamber (namely carbon/graphite) during the HIP treatment frequently results in a slight darkening of the part and the presence of a smoky color, even when measures are taken to avoid such contamination by covering the part with a blanket of molybdenum foil. Recent work at TA&T has shown that in some cases this discoloration may be removed by performing an annealing stage in oxygen following the HIP treatment. In this treatment, pure oxygen was pumped into the furnace while the dome sat in the furnace at a temperature of approximately 1000°C for extended periods of time. These temperatures are not sufficient to cause considerable grain growth, but are sufficient to oxidize the adsorbed carbon from the surfaces of the dome, reducing the grey color of the dome and improving overall clarity. To quantitatively determine the overall improvement in transmission caused by the annealing step, and to determine the optimal post-HIP annealing treatment, a matrix of anneal conditions will be tested, shown below in Table 4. One, 1 inch diameter core from each 3 inch diameter dome will be removed prior to annealing to allow for quantitative comparison of the transmission spectra from both samples.

Table 4: Matrix of Annealing Conditions

Temperature (°C)	Duration (hrs)	Atmosphere
1000	5	Air
1000	10	Air
1100	5	Air
1100	10	Air
1000	5	Oxygen
1000	10	Oxygen
1100	5	Oxygen
1100	10	Oxygen

### Task 5: Grain growth inhibitors

After the difficulty of sintering to optical clarity, the greatest challenge to optimizing the materials properties is minimizing the grain size. Hot pressing (and pressureless sintering followed by HIPing also) leads to exaggerated grain growth that reduces the overall strength of the part. One strategy for reducing the overall size of grains is the finished part is pinning of grain boundaries. Very small insoluble particulate second phases can be introduced into the spinel powder prior to sintering to inhibit grain growth. If grain boundary pinning particulates are small enough, typically nanoscale, they will not affect the optical transmission of the part, and may therefore be used to inhibit exaggerated grain growth. Prior work with spinel suggests that cerium oxide may be one potential candidate to pin grain boundary movement during sintering.<sup>†</sup> Other potential candidates, like SiC exist and can also be included.

### Subtask 5.1: Grain Boundary Pinning Strategies

#### *Subtask 5.1.1: Cerium Oxide Pinning of Grain Boundaries*

Cerium oxide ( $\text{CeO}_2$ ) has a face centered cubic structure and melts at approximately 2500°C, which is higher than the melting point of spinel. As such, it is likely to remain stable and is one potential phase suitable for pinning of grain boundaries. Due to difficulties with agglomeration that can arise with nanopowders that would make homogeneous distribution of nanosized cerium oxide very difficult, introducing it directly as a particulate is not favored. However, cerium nitrate ( $\text{CeNO}_3$ ) is water-soluble and oxidizes to form cerium oxide during sintering in air. Dissolving the cerium nitrate in water and mixing with the powder batch would produce a residue of the reactive nitrate in grain boundaries. Subsequent sintering will be used in an attempt to produce nanodispersed cerium oxide in the grain boundaries, subsequently pinning grains. The same concentrations of cerium nitrate as those proposed in Subtask 5.4.1 (0.001 wt%, 0.01 wt%, 0.05 wt%, 0.1 wt%, and 0.2 wt%) will be tested for their ability to pin grain boundaries. The same sintering cycles (1550°C for 2 hours or 10 hours, 1650°C for 2 hours or 10 hours) will be used for these parts, and compared against samples fabricated from unmilled powder.

<sup>†</sup> Don Roy – personal communication.



#### *Subtask 5.1.2: Silicon Carbide Placement in Grain Boundaries*

Starfire is a pre-ceramic polymer that decomposes on heating in an inert atmosphere to silicon carbide. Optimum conditions may vary depending on furnace size and design, but in general, the material requires two separate steps, curing and pyrolysis. As a polymer, the substance may be dissolved into hexane and combined with spinel powder. After mixing sufficiently by ball milling or shaking, the powder is dried to remove the organics and then cured to form the SiC. Crosslinking takes place at around 400°C, while pyrolysis occurs at 850°C. During the normal burnout schedule, performed at 700°C, these temperatures will be sufficient to cause formation of amorphous silicon carbide, producing an anticipated dispersed nanophase particulate in the grain boundaries before sintering takes place at 1550°C. The dried and cured powder will be ball milled and sieved to ensure that any large agglomerates are removed. In order to ensure that a variety of silicon carbide loads are placed into the samples, five different weight percentages will be tested, 0.001 wt%, 0.01 wt%, 0.05 wt%, 0.1 wt%, and 0.2 wt%. At least four samples from each concentration will be produced for use in this sintering study. In order to qualitatively demonstrate the effect of grain boundary pinning produced by the incorporation of silicon carbide, a set of four control samples will also be fabricated without binder. One sample from each group, including the control samples, will be sintered at 1550°C using the standard protocol time of 2 hours. In addition, one set of samples will be sintered at 1550°C for 10 hours. Two sintering cycles will be performed at 1650°C for the same durations as those performed at 1550°C to compare the effect produced by increased temperature. Grain growth typically follows Arrhenius type behavior, and sintering studies at these elevated temperatures will test the grain boundary pinning capabilities of the incorporated silicon carbide.

#### **Subtask 5.2: Transmission Measurement and Microstructure Analysis of Candidate Materials**

In order to understand the contribution of second phase additives to the spinel microstructure, coupon sections from each sample will be polished and examined by optical microscopy. While the intended nanoscale phase present in the grain boundary will not be observable in the optical microscope, agglomerates and micron-scale particulate, if present, will be easily recognized. In order to examine grain boundaries for the presence of nanoparticulates, high resolution scanning electron microscopy will be used to look at the same polished sections.

#### **Subtask 5.3: Strength Testing of Candidate Materials**

Since opaque microstructures do not bring us closer to the goals of this investigation, materials produced in Subtask 5.1 that are opaque will not be tested for flexure strength. However, materials that are transparent or nearly transparent after HIPing will be fabricated as larger plates by uniaxially pressing candidate powders in 5" diameter dies, followed by the normal processing methods. Chand Associates will fabricate the flexure bars for flexure testing, and Orton will test the flexure strength of all candidate materials. The most promising additive concentration from Subtasks 5.1.1, 5.1.2, and 5.1.3 will be fabricated in larger plates for strength testing.

#### **Task 6: Determination of Fundamental Optical and Materials Properties**

Grain size, impurities, and processing conditions may affect critical design characteristics of high temperature optical materials. Many of these relevant quantities, such as emissivity, absorption coefficient, index of refraction as a function of wavelength and temperature, and dielectric constant have been measured before, but by other groups working with different starting powders

and different finished grain sizes.<sup>1</sup> In order to advance the understanding of the relationship between processing conditions and optical/mechanical characteristics, a fundamental study to determine these materials characteristics for various sintering conditions is proposed. TA&T will work with the JCM contractor to establish specific performance criteria and deliver several finished dome blanks to the contractor for testing to these specifications.

#### **Subtask 6.2: Other Materials Characteristics**

Orton Materials Testing and Research is a leading service lab for the characterization of ceramic physical properties. Orton will provide basic physical property data such as hardness, flexural strength, coefficient of linear thermal expansion, thermal conductivity, and specific heat. At the conclusion of this subtask, both the optical and physical properties required for designing optical components with spinel will have been determined, contributing directly to the commercialization potential of the material in the marketplace by giving designers the necessary quantities to use spinel in optical components.

#### **Subtask 6.3: Rain and Dust Erosion**

Hemispherical domes and windows must also provide durability against rain and dust erosion. The goal of rain and dust erosion testing is to determine the impact velocity damage threshold as a function of microstructure and processing conditions. Only then can conformance to system specific requirements and quality assurance specifications be assured. Spinel coupons of 0.25 in minimum thickness will be tested at varying velocities in a rotating whirling arm water jet rig for multiple impact endurance tests. Possible fatigue effects at velocities below the single impact velocity damage threshold can be determined from the longer exposure endurance tests. All tests will be videotaped. At least two of these rain erosion endurance tests will be performed. A 2 hour test will be performed at a speed of 500 MPH, followed by a second test performed for 2 hours at a speed of 700 MPH, unless more suitable conditions are specified by the program office.

Suspended sand concentrations mean particle radii and 3 sigma standard deviations for heavy, medium, and light aerosol loadings as defined by the Air Force Advanced Infrared Search and Track (AIRST) program will be used as the basis for worst case dust environment tests at various altitude bands. Previous programs have compared damage in test coupons to damage in windows removed from the field and found that large particle tests best reproduce field damage. Damage to a brittle material, such as spinel, is expected to vary with the square of the energy of the particle impact, or as the fourth power of the velocity. In consideration of the strong velocity dependence, most of the damage will accrue during the final high-speed portion of the takeoff cycle. Based on the above rationale, two velocities, two mean particle diameters, and two mass loadings will be used for testing erosion behavior of spinel coupons. Post-test characterization of rain and dust erosion specimens will include visual inspection, photographic documentation, FTIR spectral measurements, and ring-on-ring residual strength measurements. These results will be correlated with microstructural-processing data to determine the best combination.

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<sup>1</sup> D.W. Roy and J.L. Hastert, Proceedings of the 7<sup>th</sup> Annual Conference on Composites and Advanced Ceramic Materials, Cocoa Beach, FL, 1983.

## **Task 7: Index Matched Glass Coatings**

The difficulty of grinding and polishing transparent spinel domes contributes to a high overall cost of a finished dome blank. One method of partially reducing these costs would be the successful application of an index matched glass coating, which would be applied to the inside of the dome blank. The outer surface is considered a leading edge on the aircraft and subject to substantial erosive forces which necessitated the hard transparent spinel material in the first place. A glass coating on this surface would not be suitable. The coating would be applied to the interior surface of the dome and the glass is significantly easier to polish than the spinel. Thus, grinding and polishing time may be minimized reducing finishing time and therefore cost. As such, providing assistance to, and analyzing coatings from glass coating companies are worthy objectives of the Phase II effort which directly affect the cost of spinel, and its commercialization timeline and potential. TA&T has made several glass producers aware of the importance of this objective, and they are currently in various stages of research geared towards producing index matched glass coatings for TA&T. It is these coatings that will be evaluated as a part of the Phase II effort.

### **Subtask 7.1: Prepare Samples and Analyze Transmission Data**

In order to quantitatively understand the effect of adding a glass, standardized samples must be fabricated, ground, polished, or semi-polished, and their transmission measured in the ultraviolet/visible wavelengths. For the purposes of this task, these samples will be pressed using a standard CIPing, sintering, and HIPing protocol. The objective of this task is to determine whether a glass coating can be used to substitute for the final polishing steps as a cost saving measure. A variety of samples will be provided to various coating companies with one polished face and one ground or semi-polished face (for example, to a surface finish of 15 micron or 30 micron) to be coated and compared with an archival sample polished on both faces.

## **Task 8 Preparation and Testing of 7" Domes: Homogeneity, Strength, and Microstructure**

Through the completion of Tasks 1 through 4, the optimal sintering and HIPing conditions will have been determined, as well as the ideal binder content and feasibility of incorporating second phases in the microstructure to pin grain boundaries. The optimal conditions will be used to produce a series of 7 inch diameter domes for examination of characteristics such as homogeneity (throughout the dome), strength, and grain size, as well as rain erosion and aerothermal loading tests.

### **Task 9: Final Report**

A final report will be prepared to detail the results of this comprehensive study. The complete processing window will have been determined at the conclusion of this study, including the sintering and HIPing conditions necessary to produce optically transparent parts with the minimum grain size achievable using conventional sintering methods. The results of all grain boundary pinning studies will be detailed, as well as the results of all strength testing on these candidate materials. The results will be a complete picture of the processing window capable of producing transparent spinel domes, measurement of the grain sizes for these conditions, and quantitative comparison of the strengths of these materials.

## **7. Conclusions**

In this Phase I effort, Technology Assessment and Transfer demonstrated the feasibility of a pressureless sintering approach for fabricating transparent, hemispherical dome blanks for the Joint Common Missile (JCM). This effort encompassed work in the refinement of powder processing methods and techniques, determination of a suitable sintering profile and atmosphere (vacuum), and exploration of the processing window for hot isostatic pressing to transparency. The primary challenge remaining in the fabrication of the dome blanks is the elimination of speckles in the finished blank by improved spray drying formulations. It is anticipated that in the Phase II effort, transparent, entirely defect free dome blanks will be reproducibly fabricated, and their mechanical and thermal properties will be studied in more detail.